FACULTY OF SCIENCES

# SELECTIVE MULTI-ELEMENT ANALYSIS OF THE CLAY FRACTION IN ANCIENT POTTERY BY LASER ABLATION – INDUCTIVELY COUPLED PLASMA – MASS SPECTROMETRY

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## Introduction

In the past two decades, laser ablation–inductively coupled plasma–mass spectrometry (LA-ICP-MS) has become an interesting alternative to the bulk solution methods for elemental analysis of pottery clay with the aim of provenance determination.

| Advantages | Challenges |
|---|---|
| No digestion step | Direct solid sampling without internal standard |
| Spatially resolved analysis | Limited amount of clay reference materials |

The current study investigates the capabilities and limitations of selective LA-ICP-MS analysis of the clay fraction in thin sections of sediments and pottery in comparison to those of the more common bulk analysis techniques.

Fig. 1 Partially reconstructed flask from the site Spiere-de-Hel[1]

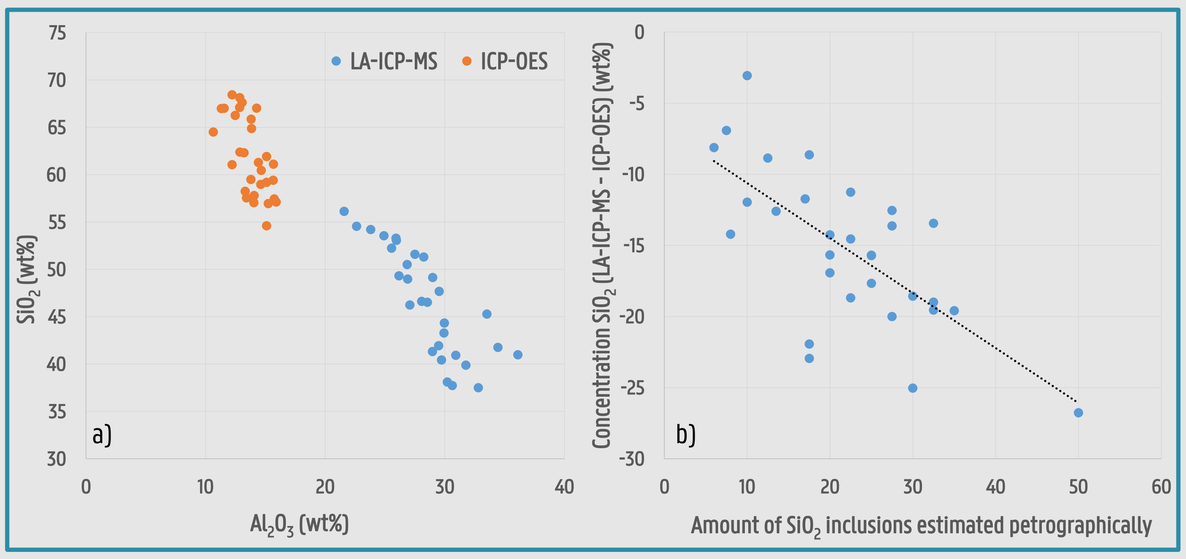


Fig. 4 a) Scatterplot with the concentrations of $SiO_2$ and $Al_2O_3$ in 30 thin sections from Spiere-de-Hel as obtained using LA-ICP-MS and ICP-OES, b) difference between $SiO_2$ concentration in 30 thin sections of pottery from Spiere-de-Hel as obtained using LA-ICP-MS and ICP-OES as a function of the petrographically estimated amount of $SiO_2$ inclusions.


Fig. 2 a) pressed pellet (Ø=13mm), b) sherd after thin sectioning, c) thin section

## Materials and methods

1) A pressed, baked and polished pellet of NIST SRM 679 Brick Clay has been analysed repeatedly by LA-ICP-MS and the data was processed with different calibration approaches based on a calibration set of glass standards. The elemental concentration results were compared with the reference values from the GeoRem database[3].

2) The clay fraction in 30 thin sections of pottery from the middle Neolithic site 'Spiere-de-Hel' has been analysed by LA-ICP-MS and the results are compared to those obtained in previous bulk analyses of the same pottery by inductively coupled plasma – optical emission spectroscopy (ICP-OES).[1,2]

The Instrumentation used for the LA-ICP-MS analyses consists of an Analyte G2 ArF*excimer-based-deep UV laser system from Teledyne Cetac Technologies and an Xseries II quadrupole-based ICP-mass spectrometer from ThermoScientific.

## 1) Choice of calibration method

Differences in ablation behaviour between clay material and glass cause concentration values that are systematically biased when using external calibration without internal standard (IS) correction. A sum normalization approach whereby the concentration of Si as internal standard is initially estimated to be 30 weight percent (wt%) and is afterwards corrected by assuming the sum of all oxide concentrations to be 100 wt% produces nearly identical results as an external calibration approach whereby the bulk Si concentration from the certificate is taken as IS.

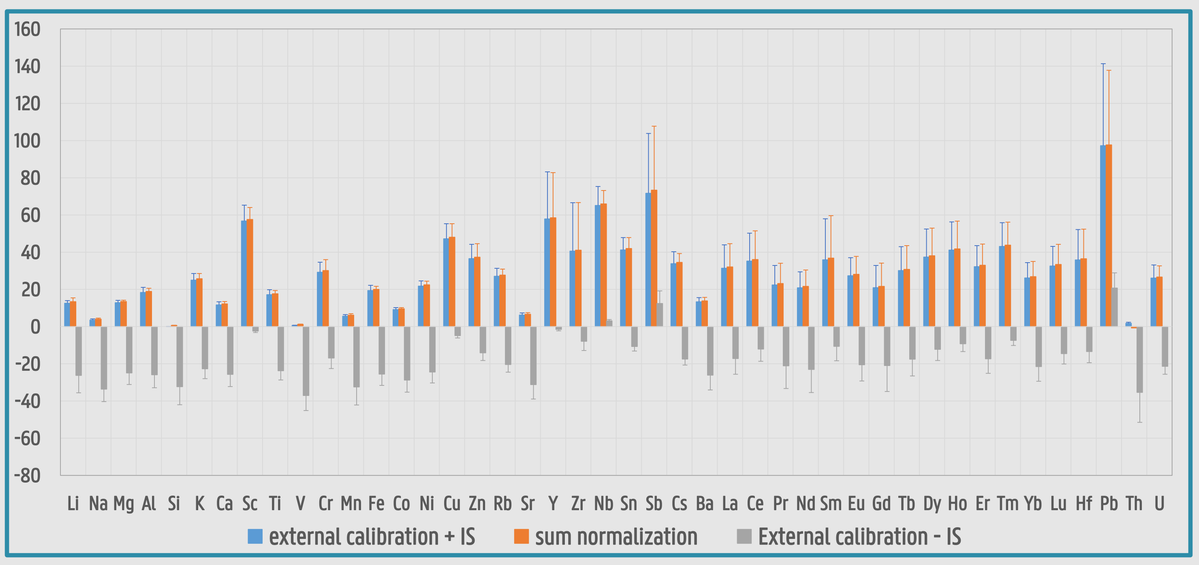


Fig. 3 Bias between the results obtained for a pressed pellet of NIST SRM 679 and the corresponding GeoReM reference values.[3]

## 2) The use of thin sections

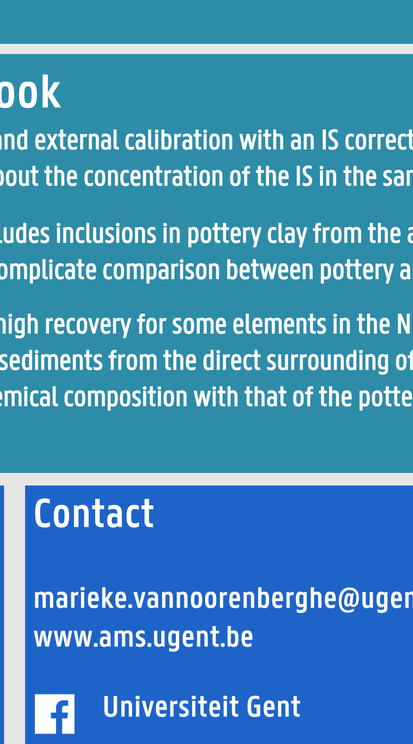


Fig. 5 Typical microphotograph of a thin section of the pottery from Spiere-de-Hel.[1]

Middle Neolithic pottery consists of multiple fractions forming a very heterogeneous material. Non-clay fractions can be added by the potter (temper) or can be naturally present in the sediment. In the pottery from the site Spiere-de-Hel, chunks of flint have been added by the potter and form the most prominent inclusions. Inspection of the $SiO_2$ concentration in 30 pottery sherds from Spiere-de-Hel as obtained by LA-ICP-MS reveals a systematically lower concentration for $SiO_2$ compared with previous bulk-ICP-OES analyses. The concentrations of other elements are accordingly higher because of the dilution effect. The difference of $SiO_2$ concentration between the two techniques correlates with the amount of petrographically estimated $SiO_2$ inclusions (chunks of flint and quartz grains in the sand/silt fraction).

## Conclusions and outlook

1) The sum normalization approach and external calibration with an IS correction provide similar results. This implies that upfront knowledge about the concentration of the IS in the samples is not crucial.

1) LA-ICP-MS analysis effectively excludes inclusions in pottery clay from the analysis. This implies that temper added by the potter which could complicate comparison between pottery and sediment can be avoided.

Future research will shed light on the high recovery for some elements in the NIST SRM 679 Brick Clay. In addition, LA-ICP-MS analysis on thin sections of sediments from the direct surrounding of the site Spiere-de-Hel will be performed in order to compare the chemical composition with that of the pottery to answer hypotheses of plausible provenance.

## References

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